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TECHNICAL PAPER

ISSN 1047-3289 *J. Air & Waste Manage. Assoc.* **53**:000–000

Tank Atmosphere Perturbation: A Procedure for Assessing Flashing Losses from Oil Storage Tanks

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ABSTRACT

A new procedure to measure the total volume of emissions from heavy crude-oil storage tanks is described. Tank flashing losses, which are difficult to measure, can be determined by correcting this value for working and breathing losses. The procedure uses a fan or blower to vent the headspace of the storage tank, with subsequent monitoring of the change in concentrations of oxygen or other gases. Combined with a separate determination of the reactive organic carbon (ROC) fraction in the gas, this method allows the evaluation of the total amount of ROC emitted. The operation of the system is described, and results from measurement of several storage tanks in California oil fields are presented. Our measurements are compared with those obtained using the California Air Resources Board (CARB) 150 method.

INTRODUCTION

There is concern that reactive organic carbon (ROC) (C3 and higher) emissions from heavy crude-oil storage tanks contribute significantly to the burden of organics in regional air basins. As a result, the heavy oil storage tank (HOST) committee was established to assess tank emissions and measurement procedures for oil fields in California. The HOST project is a joint effort of California and federal agencies, the Western States Petroleum Association, and the Lawrence Berkeley National Laboratory. The project goals include assessing existing methods for determining tank emissions and the development of new, scientifically sound methods where needed.

> **IMPLICATIONS**
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> Existing methods usually fail to accurately measure or predict emissions from heavy crude oils. The method described here determines the total volume of gas emitted to the atmosphere. When combined with an independent measurement of the ROCs, it can be used by industry and regulators to provide quantitative information for emissions inventories and regulation development and enforcement.

The ROC emissions from a storage tank depend on the concentration of ROCs in the tank headspace and the rate of venting of headspace gases. There are three mechanisms that produce venting of headspace gases:

(1) working losses, caused by changes in the liquid level in the tank;

(2) breathing losses, caused by diurnal heating and cooling of the headspace volume, with associated movement of gases out of and into the headspace; and

(3) flashing losses, caused by gases evolving from the oil in the tank.

The total headspace gas vented from a tank is the sum of these three factors. In constant-level tanks, working losses are generally small and breathing and flashing losses dominate venting. Working loss and breathing loss are readily calculated from the change in oil level and changes in headspace temperature, respectively. The U.S. Environmental Protection Agency maintains the AP-42 documents, which describe calculations for predicting working and breathing losses from storage tanks.[1] In addition, a PC program, TANKS, is available to perform AP-42 calculations for storage tanks.[2]

Until now, there has been no straightforward method to assess flashing losses for heavy crudes, which often have high levels of water associated with the oil and can be stored at temperatures in excess of 180 °F. Gas emissions from tanks containing produced heavy crude oil were observed for several days, so gas:oil ratios derived from short-term or equilibrium measurements may not provide accurate values. Also, a few wash tanks have gas: liquid separators upstream where some of the flashing gas may be removed. The California Air Resources Board (CARB) attempted to use an established procedure (the CARB 150 method) to measure tank emissions over a 24-hr period. This method, developed for gasoline-like liquids, uses large integrating flow meters (e.g., turbine meters) attached to a tank hatch to measure the flows in and out of a tank and includes monitoring and GC analysis of the headspace gases.[3] The method is difficult to implement and requires the tank to be well sealed and have accessible hatches and vents. The system must be monitored continuously for 24 hr. Only a very limited number of CARB 150 measurements have been performed on tanks that contain other liquids, such as heavy crude oil, where significant amounts of water, CO_2, and methane may be present.

An alternative procedure to the CARB 150 method that is faster, more accurate, much easier to implement, and can be applied to tanks that are not readily sealed to the ambient air was developed. The procedure is called the tank atmosphere perturbation (TAP) method. The concept behind the method is to rapidly add ambient air to the tank headspace so the headspace gas concentrations are perturbed and then monitor the change in concentration of oxygen and other compounds as the flashing gas replaces the air. From the rate of change in concentration with time, the rate and quantity of gas flashing out of the oil can be inferred. If desired, the contribution of the different loss modes can be assessed by calculating working and breathing losses using well-established methods.

PROCEDURE

The TAP method depends on perturbing the headspace gas composition. This is accomplished using a variety of techniques to introduce air into the tank headspace. In some cases, sufficient perturbation was obtained by opening one or more of the tank PV hatches. A combination of wind and temperature differential between the ambient air and the tank headspace was sufficient to significantly alter the concentration of gases in the headspace. Most of the measurements were made using fans to introduce air. For small tanks, a gasoline-powered leaf blower (250 cfm) was sufficient to ventilate the headspace. An explosion-proof electric fan with a 1.5-hp motor (9000 cfm) was used for larger tanks. The headspace volumes were typically ventilated for 30–60 min, which was sufficient to reach oxygen levels near that of air. The time needed was also estimated by measuring the fan flow rate and allowing sufficient time for 10 exchanges of the headspace volume. Oxygen concentrations were measured with a Gas Tech GT201 portable electrochemical oxygen analyzer. Samples also were collected periodically in evacuated bulbs for later gas chromatographic analysis to determine the concentrations of oxygen and other gases.

Because potentially flammable or explosive mixtures may result, it is imperative that proper safety precautions are taken, including proper grounding of all components. Similar flammable conditions were observed during routine operation in some tanks where periodic liquid level changes draw into the headspace air with a high methane concentration, so all headspace gas should be treated as flammable unless a determination otherwise is made with appropriate instruments.

After the vapor space is purged with air, the gases evolving from the tank liquids dilute the air, and the resulting gas mixture flows out of the PV hatch. However, purging will cool the headspace if the ambient temperature is lower than the normal headspace temperature. The headspace gas will heat up during and after venting, and the fraction of water vapor in the headspace will increase as it saturates with water vapor. This occurs in the first few minutes after venting, and the oxygen measurements made shortly after venting are not very useful.

If the flashing rate is reasonably constant and the mixing is rapid (perfectly stirred reactor assumption), the decrease in oxygen concentration with time can be treated as a first-order decay:

$$\mathrm{d}[A]/\mathrm{d}t = -k[A] \quad \text{or, in integrated form,}$$

$$\log_e[A]/[A_{(t=0)}] = -kt \quad (1)$$

where A represents the tracer gas (oxygen) concentration, t is time, and k is the first-order decay rate constant. The decay rate is used to infer the rate of evolution of flashing gas. Corrections must be applied in cases where there is a change in liquid level or the tank is not well sealed. These situations are discussed later.

EXPERIMENTS

Several different heavy oil storage tanks in the Kern River field near Bakersfield, CA, were used in this study. Typically, there are several tanks in a series, where the oil/water mixture is separated, with the oil piped from one tank to another tank for additional processing or shipping. The tanks operate at atmospheric pressure, with pressure/vent hatches to prevent more than a few inches of water pressure or vacuum. The storage tanks that were used in this study are listed in Table 1. All of the tanks T1
contained heavy crude oil (API gravity 12–14) and produced water. Previous research[4] determined that the headspace gas species in these tanks consists of CO_2, methane, water, and air. The gas emitted from the oil is mainly CO_2 and methane; water vapor is in equilibrium with the liquid water (the water fraction is as high as 90% in some tanks), and air is from leaks or breathing or working losses. The baseline oxygen concentration in the tank headspace was measured, and then the tank was vented until the headspace oxygen concentration was close to the ambient concentration. The oxygen concentration was checked periodically until it approached the concentration measured before venting. The data were then analyzed to assess the tank emissions.

CARB 150 measurements also were performed on several wash and shipping tanks. This method uses flow-measuring equipment to replace the vacuum/vent valve.

Table 1. Tank properties.

Tank	Tank Volume (bbl)	Diameter (ft)	Height (ft)	Liquid Temperature (°F)	Tank Condition
Surge 1 wash	37,599	80	48	140	Sealed
Surge 3 wash	37,599	80	48	140	Leaks
Surge 5 wash	37,599	80	48	140	Leaks
Cauley wash	3456	34	24	135	Sealed
Cauley shipping	864	21	16	135	Sealed
Frank wash	1621	24	23	110	Sealed
Torch MS LACT	1500	22	22	77	Leaks
Chevron 3-1	10,000	59	21	155	Sealed
YMK wash	4377	39	24	147	Sealed

All of the gas entering or leaving the headspace is routed through integrating flow meters to determine the total flow out of the tank headspace. This method was developed for gasoline storage tanks, and it has never been applied to heavy oil-storage tanks before the HOST study.

Two gas chromatographs were used to analyze the composition of the bulb samples. An SRI 8610 gas chromatograph with a TCD and a 1/8″ × 12 ft. Porapak Q column using helium carrier was used to measure air, methane, and CO_2. The column was replaced with a 1/8″ × 6 ft 5A molecular sieve column to measure oxygen and nitrogen. An HP 5880A gas chromatograph with an FID and a 0.32 mm × 20 m Astec Gaspro GSC PLOT column with backflush was used to measure C_1–C_{10} hydrocarbons. The sample loops of the instruments were connected in series so they could be filled simultaneously from the bulbs. The instruments were periodically calibrated with standard gas mixtures (10% methane in nitrogen and 11% CO_2 in argon from Matheson, and a 1000 ppm C1–C6 in nitrogen from Scott Specialty Gases). Periodic calibrations were used to compensate for any changes in the response of the chromatographs.

RESULTS AND DISCUSSION

The tank headspaces are generally well mixed because of the convective flow generated by the difference in the oil pad and headspace gas temperatures. Wash tanks with fairly constant production rates and shipping tanks with small changes in their liquid level are best suited for such treatment. The volume of the headspace is readily calculated from the tank geometry and oil level, and the ROC concentration in the tank headspace can be determined by a number of methods.[4] With this information, the rate constant times the headspace volume (either the total or corrected volume, as discussed in the next section) determines the total flow out of the tank. The total flow out multiplied by the ROC mole fraction in the headspace yields the ROC emission rates.

Oxygen is a convenient gas to use as a tracer species. It can be used when the headspace is not initially filled with air. Handheld oxygen meters can be used to perform measurements on the gas flowing out of the tank, avoiding the need for a mobile laboratory. Nitrogen is not as suitable as oxygen, because measurements of nitrogen:oxygen ratios in some tanks indicate that nitrogen is a trace component of the flashing gas or that nitrogen is used as a blanket in certain oil field operations. The nitrogen:oxygen ratio increased with time, and the decay of nitrogen did not approach zero for some of these tanks. Analysis of flow behavior using gases evolving from the produced oil, such as methane and CO_2, is more complicated because both flow in and flow out terms must be considered.

Corrections to Tank Headspace Volume

When using oxygen or other gas as a tracer, care must be taken in using the proper headspace volume in the calculation. The temperature and pressure must be corrected to standard conditions. If the gas concentration measurements are made on a dry basis (e.g., when an unheated tube is used to transport the headspace gas to a monitor or a trap in an ice bath is used to remove condensable water), then the headspace volume should be the dry volume. The concentration of the water vapor is determined by measuring the headspace temperature and assuming that the water vapor is in equilibrium with liquid water. However, if an oxygen monitor is used to measure oxygen as a percentage of the entire gas (including water vapor) at the headspace temperature (so no condensation occurs), the total headspace volume is used in the calculation. The following equation incorporates the corrections to the headspace volume:

$$\text{Corrected Volume} = \text{Actual Volume} \times (520°\text{R}/T_{\text{headspace}}) \times (\text{Actual pressure}/14.7\ \text{psia}) \times (1 - \text{water vapor fraction}) \quad (2)$$

In tanks with no significant wind-driven air intrusion and an initial concentration of oxygen near zero, the decay of oxygen concentration in wash tank headspaces after venting will display first-order decay behavior. This behavior was observed for well-sealed tanks or those with oil that has significant amounts of dissolved gas, where flashing losses dominate. Figure 1 shows a plot of the natural log ($\log_e$) of the oxygen concentration versus time for a tank that was sampled by several different methods. This tank F1

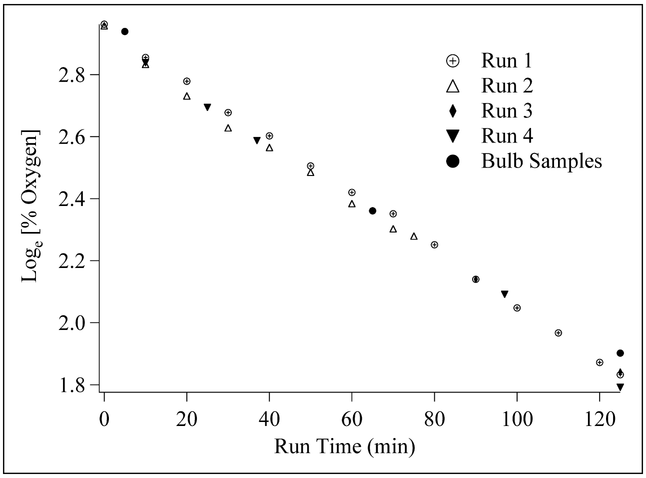

Figure 1. Plot of log$_e$ (% oxygen concentration) vs. time following venting for a 37,600 bbl wash tank with a 23,700 ft^3 headspace volume.

was 80 ft in diameter and 48 ft high and contained 37,600 bbl liquid. The tank headspace was vented for 60 min with a 9000-cfm electric fan, and the oxygen concentration was monitored with three systems. The gas venting out of the headspace was periodically monitored with the handheld oxygen analyzer and by filling evacuated bulbs. The gas in the headspace was also continuously monitored with oxygen and CO_2 analyzers in a mobile laboratory. The sampled gas was drawn through a cold trap in an ice bath before flowing to the analyzers, resulting in a dry gas concentration. The oxygen concentration declined substantially during monitoring for several hours. The headspace was then vented again, and the monitoring was repeated. No bulb samples were collected during the second monitoring run. The five measurements, plotted in Figure 1, show excellent agreement with one another. The average flow out rate constant obtained from the measurements is 0.0087/min. The headspace volume was estimated to be 23,700 ft^3, the headspace temperature was 110 °F, and the ambient pressure was 14.5 psi, so the corrected dry headspace volume was 19,500 scf. The resulting flow rate is 170 ft^3/min (at 60 °F and 1 atm).

Tanks that are not well sealed or that have faulty or leaking hatches can be susceptible to wind-driven injection of air. Such leaks prevent the use of other methods, such as the CARB 150 method, to determine the gas flow rates because they require that all the gas evolved pass though flow-metering equipment. In the TAP method, the airflow into the headspace caused by wind can be treated as a constant, with the ratio of airflow in to flashing gas emitted derived from the ratio of oxygen concentration in the headspace to the oxygen concentration in ambient air (20.9%). The behavior of gases in a tank headspace with air intrusion is shown in Figure 2. The tank under study had a hatch with a cover that did not close completely and was upwind of another vent also open to the atmosphere. The opening in the hatch affected the venting operation as well as the recovery from the perturbation. During the venting of the headspace, some of the air injected into an adjacent hatch by the fan flowed out of the partially open hatch before it could completely mix with the headspace gases. After the headspace was vented by the fan, air continued to flow into the headspace. This limited the change in concentration of the gases. From the steady-state concentration of oxygen (9.25%), the fraction of the gas flowing out of the tank because of air intrusion when the fan is off can be calculated:

F2

$$9.25\%\ O_2 \text{ in vented gas}/20.9\%\ O_2 \text{ in air} = 0.44 \quad (3)$$

A log$_e$ plot of the oxygen concentration in tanks with air intrusion will not yield a linear plot. However, if the steady-state oxygen concentration is subtracted from the values of oxygen measured following the tank ventilation with a fan, reasonably linear plots are observed, with their slope used to estimate the venting rate. In the case of the tank mentioned previously, the slope of the plot of loge [O_2]corr versus time yields a slope of approximately 0.014/min. There was some variation in the wind during the sampling time, which caused variations in the plotted data.

If there is a steady airflow into the tank, the composition of the headspace gas will depend on the ratio of the flow of air and the flow of gas out of oil.

$$[O_2] = \text{flow(air)}/[\text{flow(air)} + \text{flow(oil)}] \times [O_2]_{air} \quad (4)$$

If the flow of air into the tank headspace is increased by using a fan to blow air into the tank, excess oxygen will be

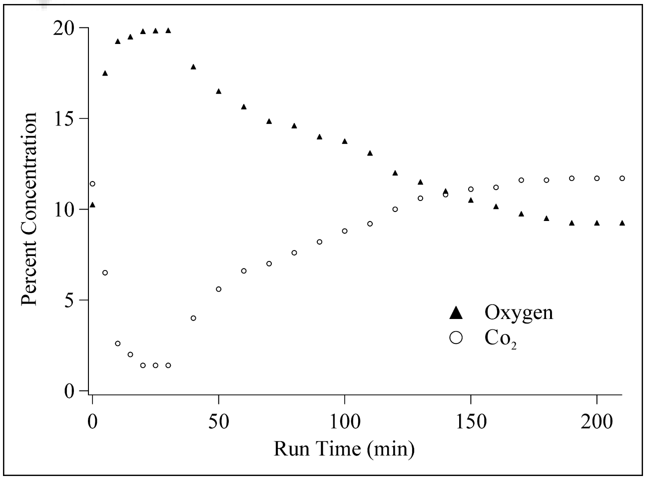

Figure 2. Plot of oxygen and CO_2 concentrations with time in a tank with air intrusion into the headspace. Tank dimensions were similar to the tank monitored for results shown in Figure 1.

added above the unperturbed concentration. The new equilibrium concentration of oxygen in the headspace will be

$$[O_2] = \text{flow(total air)}/[\text{flow(total air)} + \text{flow(oil)}] \times [O_2]_{air} \quad (5)$$

Alternately, one can consider the oxygen added by the fan to be a different species than the oxygen added by the wind.

$$[O_2]_{total} = [O_2]_{fan\ (or\ excess)} + [O_2]_{unperturbed} \quad (6)$$

When the fan is stopped, the oxygen concentration will decay back to the initial unperturbed level. The rate of decay will depend on the flow out of the tank, as before. The excess oxygen displays an exponential decay back to the initial oxygen concentration. If the unperturbed oxygen concentration is subtracted from the total oxygen concentration, the residual should be the excess added by the fan. A natural log plot of this quantity versus time yields the flow out rate constant.

A Note on "Constant-Level" Tanks

Tanks that are operated as constant-level tanks often have small variations in the overall liquid height inside the tank caused by variations in the liquid flow rate or cycling of pumps connected to the tank liquid. Small changes in the liquid level can have a significant effect on the headspace volume. For example, a 1-in. drop in the liquid level in a 30-ft-diameter tank will increase the headspace volume by approximately 59 ft^3. The associated drop in pressure in the headspace is often sufficient to activate the vacuum side of the PV hatch and pull outside air into the tank headspace. Periodic changes in liquid height in a constant-level tank can introduce air into the headspace so the oxygen concentration is significantly higher than what it would be if the tank were maintained at a truly constant level. This will not interfere with the TAP measurement as long as the oxygen concentration can be perturbed from the level found in the tank. The TAP method can be used on a tank with a headspace that is connected to the headspace of another tank when proper precautions are taken. It is necessary to insure that gas from the other headspace does not flow into the headspace under test and increase the apparent flashing rate. This can be done by creating a small opening through which the adjacent tank headspace can vent.

The TAP method can be adapted to tanks that undergo significant changes in liquid level during measurement, such as shipping tanks. Air is generally pulled into the tank headspace when the oil is shipped out of the shipping tank and the liquid level drops, and the oxygen concentration is changed. If the tank is being filled during measurement, the volume of liquid that supplies the flashing gas increases while the headspace volume decreases. If the filling time is significantly longer than the measurement time, the same equations will hold. More rapid filling can be handled by adding a term that reduces the headspace volume with time. However, it should be noted that the amount of liquid in the tank does change during the measurement. The TAP method is not suitable for tanks with vapor recovery systems, although such tanks generally do not have significant ROC emissions.

The venting analysis could be applied to some of the tanks tested previously using the CARB 150 procedure. During the set-up process for a CARB 150 measurement, hatches were opened to mount flow meters and sampling systems. In some cases, there was sufficient venting of the headspace to significantly increase the oxygen concentration during this period. The concentrations of headspace gases, including air, were monitored as part of the CARB 150 procedure. Oxygen and nitrogen were not measured separately in most of the CARB 150 tests, because air was measured as a single GC peak. The oxygen concentration was estimated by multiplying the concentration of air by 0.209. A $\log_e$ [O2] versus time is shown in Figure 3 for a well-sealed wash tank. This tank was significantly smaller than the tanks discussed previously (4400 bbl, 39-ft diameter, 24-ft high), and air was vented out of the headspace more slowly. The flow out rate constant was determined to be 0.00107/min. With a measured headspace volume of 3000 ft^3 (2520 corrected), an average corrected flow rate of 161 scf/hr is calculated. F3

For comparison, the CARB 150 measurement using flow meters to measure the flow out of (and into) the tank yielded an average corrected flow out rate of approximately 165 scf/hr. For this tank, in which no leaks were

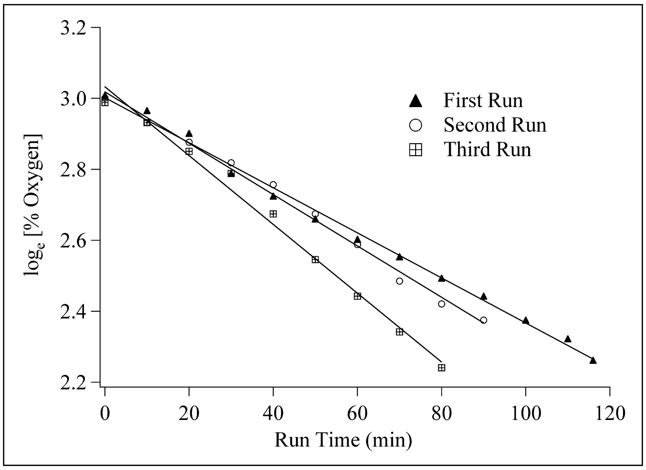

Figure 3. Plot of $\log_e$ (% oxygen concentration) vs. time in a wash-tank headspace following installation of the flow measurement system.

Table 2. Results of TAP testing.

Tank	Headspace Volume, Cor. (std ft^3)	Flow Out k (hr)	Flow Out (ft^3/hr)	$[CH_4]$ (atm)	$[CO_2]$ (atm)	[ROC] (atm)	ROC Emitted (no./day)
Surge 1 wash	19,500	0.52	10,130	0.72	0.24	1.3×10^{-3}	83.3
Surge 3 wash	19,800	0.7	13,900	0.76	0.21	[a]	
Surge 5 wash	12,800	0.61	7800	0.72	0.24	[a]	
Cauley wash	2250	0.40	900	0.62	0.25	4×10^{-5}	0.23
Cauley shipping	920	0.015	14	0.10	0.05	2×10^{-5}	1.8×10^{-3}
Frank wash	1200	0.58	700	0.84	0.02	4×10^{-5}	0.18
Torch MS LACT	1050	0.008	8	0.15	0.07	$\sim 2 \times 10^{-5}$	1.0×10^{-3}
Chevron 3-1	4370	0.071	310	0.45	0.42	1.1×10^{-3}	2.16
YMK wash	2520	0.064	161	0.63	0.18	1.7×10^{-4}	0.17

[a]Not determined.

found using visual inspection and hand-held hydrocarbon analyzers, the two methods are in excellent agreement. In the other cases where the TAP concept could be applied to tanks measured by the CARB 150 method, the TAP results generally gave larger flow out rates than do the CARB 150 measurements. In most of these tanks, there were known problems with the CARB 150 method, which allowed headspace gas to flow out of the tank without being measured by the flow meters. There problems included small holes in the tank roof, pressure-vacuum hatches that are faulty or do not seal correctly, connections between tank headspaces that are not closed, venting episodes that were too slow or rapid for the flow meters to fully respond, or condensation on flow meter blades and bearings that cause sluggish operation. The
T2 results of the TAP measurements are listed in Table 2.

Where the two methods do not agree, the TAP method is considered to be more accurate. There are fewer sources of error in the measurement procedure. It is difficult to insure that an operating tank is well sealed, that all of the gas from the tank passes through the flow meter, and that the flow meter will respond accurately under all conditions. The TAP method only requires that the tank has a significant flow out rate and that the steady-state concentrations in the tank can be perturbed.

CONCLUSIONS

A new procedure for assessing oil storage tank emissions that allows the determination of tank flashing losses was demonstrated. The method involves injecting air into the tank headspace and monitoring changes in the concentrations of the headspace gases as gas flashing from the oil dilutes the injected air. The method is much simpler to implement than existing methods and does not require a well-sealed headspace.

ACKNOWLEDGMENTS

This project was supported by the Director, Office of Fossil Energy, National Petroleum Technology Office, U.S. Department of Energy, under Contract No. DE-AC03–76SF00098. Assistance by Samuel N. Duran of ChevronTexaco and the HOST working group is greatly appreciated.

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